

TRANSLATION FROM JAPANESE

- (19) JAPANESE PATENT OFFICE (JP)
 (12) Unexamined Patent Gazette (A)
 (11) Unexamined Patent Application (Kokai) No. 5-170802
 (43) Disclosure Date: July 9, 1993

P. 6 Ca C 03
symbolical
later part

Class. (51) <u>Int. Cl.</u> ₅	Internal Office <u>Symbols</u>	<u>Registr. Nos.</u>	Technical <u>FI</u>	<u>Classification Field</u>
C 08 F 2/22	MBL	7442-4J		
C 09 D 7/12	PSM	7211-4J		
D 21 H 19/56	7199-3B	D 21 H 1/28	A	

Request for Examination: Not yet submitted Number of Claims: 3 (Total of 7 pages [in original])

- (21) Application No.: 3-340774
 (22) Filing Date: December 24, 1991
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(54) [Title of the Invention] **Hollow Emulsion Particles**

(57) [Summary]

[Composition] Emulsion particles, characterized by comprising a group of hollow particles in which voids are present inside the particles during drying, and additionally comprising a group of smaller particles; and by the fact that the particle diameter distribution is bimodal.

[Merits] The particles have excellent gloss, opacity, whiteness, drying properties, and solids concentration by weight, as well as excellent paintability and low viscosity under high shear when added to a paper coating composition (paint).

[Claims]

[Claim 1] Emulsion particles, characterized by comprising a group of hollow particles in which voids are present inside the particles during drying, and additionally comprising a group of smaller particles; and by the fact that the particle diameter distribution is bimodal.

[Claim 2] Emulsion particles characterized by having a bimodal particle diameter distribution as defined in Claim 1, wherein the particle diameter D of the hollow particles is 0.3 to 5.0 μm , the particle diameter D_s ¹ of the accompanying small particles is 0.05 to 0.3 μ , and the relation $D_s < D/2$ always holds true.

[Claim 3] A paper coating composition (paint), containing emulsion particles as defined in Claim 1.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to emulsion particles that comprise a group of hollow particles in which voids are present inside the particles during drying, that additionally comprise a group of smaller particles, and that have a bimodal particle diameter distribution, and more particularly to emulsion particles (these particles comprise a group of hollow particles in which voids are present inside the particles during drying, additionally comprise a group of smaller particles, and have a bimodal particle diameter distribution) that can be used as the pigments added to coating paints for common coated paper, paperboard, lightweight coated paper, ultra-lightweight coated paper, art paper, cast-coated paper, and other types of paper; to paints for wood surfaces, exterior walls, interior walls, and the like; and to coating agents for fax paper, thermosensitive labels, and other types of thermal printing paper.

[0002]

[Prior Art] Hard emulsion particles have been extensively studied as additives for coating agents that reduce the weight of coatings and improve their gloss, whiteness, opacity, and the like. In these applications, plastic pigments tend to be used in increasing amounts as commercial pigment substitutes for kaolin, calcium carbonate, talc, satin [white], and other inorganic pigments, particularly in the field of paper coatings.

[0003] As reported in the literature, (see, for example, (1) S. Muroi, "Paper Coatings as Applications for Polymer Plastics," Kobunshi Kankokai (1986), p. 83; (2) S. Tezuka, *Kotingu Jiho*, No. 166, p. 13 (1985); and elsewhere), polystyrene emulsion particles having uniform particle diameters of about 0.5 μ are commonly used as conventional plastic pigments. The particle diameters of such emulsion particles allow maximum scattering coefficient to be achieved, as reported by B. Alince et al. (*J. Colloid. and Interface Sci.*, **76**, 182 (1980)). The aforementioned emulsion particles, however, fail to afford the required high gloss, opacity, whiteness, lighter weight, or heat insulation in thermal recording materials. JP (Kokai) 59-59741

¹ No distinction is made between the two diameters D in the original. For the sake of clarity, the smaller diameter is indicated as " D_s " in the translation.—*The Language Service*.

discloses plastic pigments having a narrow particle diameter distribution in which 90% or more particles have a diameter of 0.20 to 0.28 μ . Such plastic pigments have somewhat better gloss but are still inferior in terms of whiteness and opacity, and are therefore impractical. Emulsion particles (so-called hollow particles) in which voids are present inside the particles during drying have therefore attracted attention as particles devoid of such shortcomings.

[0004] Such hollow particles may, for example, be manufactured by alkali swelling (JP (Kokoku) 3-9124, JP (Kokai) 64-1704, JP (Kokai) 64-48805, JP (Kokai) 1-185311, etc.), solvent addition (JP (Kokai) 61-86941, 63-135409, 1-301730, etc.), volume shrinkage (JP (Kokai) 62-127336), phase separation (JP (Kokai) 61-62510), and many other methods.

[0005] The hollow particles thus obtained, while having characteristics that vary with the manufacturing method, are nevertheless believed to have better gloss, opacity, whiteness, weight reduction, and heat insulation than so-called conventional void-free solid particles. Such hollow particles still have serious drawbacks and have so far been used on a limited scale. The first drawback is that paints containing hollow particles become much more viscous under high shear. Such paints are therefore difficult to apply and are often unusable, particularly in the field of paint coatings, where higher coating speeds have been adopted in recent years.

[0006] The second drawback is that hollow particles contain water or organic solvents when emulsified, and although the concentration of such particles by volume is not much different from that of conventional solid particles, the solids concentration by weight is lower than that of conventional solid particles. For example, concentration by weight of commercially available solid particles is commonly about 48%, but that of hollow particles is always lower (although the actual value varies with porosity). A resulting drawback is that the paint has a higher moisture content and less favorable drying properties. In addition, the commercial practice in Japan is such that the price is almost always calculated in terms of dry weight rather than in terms of the emulsion as such, so a reduction in the weight of the solid fraction leads to a higher cost and negates the advantages of hollow particles.

[0007] The aforementioned drawbacks can be overcome by reducing the volume of water or organic solvent inside the hollow particles; that is, reducing the internal particle porosity during drying, but such a reduction has an adverse effect on the aforementioned light weight, gloss, opacity, whiteness, and heat insulation of the hollow particles, and makes these particles less advantageous in comparison with solid particles. The inventors discovered that cored multilayer particles that differ from the aforementioned hollow particles, contain core particles in their interior, have a void layer in the external layer of the core particles, and possess a layer having a different refractive index are far superior to the conventional hollow particles not only in terms of gloss, opacity, and whiteness but also in terms of drying properties and many other properties.

The inventors have already filed an application (JP (Tokugan) 3-26678). The proposed solution has not been entirely successful, however.

[0008]

[Problems Which the Invention Is Intended to Solve] The present invention resides in providing practical emulsion particles that have excellent gloss, opacity, whiteness, paintability, and drying properties, and that can be used as the pigments added to coating paints for common coated paper, paperboard, lightweight coated paper, ultra-lightweight coated paper, art paper, cast-coated paper, and other types of paper; to paints for wood surfaces, exterior walls, interior walls, and the like; and to coating agents for fax paper, thermosensitive labels, and other types of thermal printing paper.

[0009]

[Means Used to Solve the Above-Mentioned Problems] As a result of thoroughgoing research aimed at addressing the above-described problems, the inventors discovered that the emulsion particles used as conventional plastic pigments have uniform particle diameters. This phenomenon appears to be based on an experimental finding that light scattering capabilities are impaired in a mixed system composed of particles having different diameters, as reported by B. Alince et al. Hollow particles manufactured by the aforementioned reported methods are commonly provided with uniform diameters. This conclusion can be easily arrived at from the detailed descriptions and working examples of the published applications. The cored multilayer emulsion particles previously proposed by the inventors are also manufactured by a method in which particle diameters are adjusted in the same way to obtain a uniform distribution. It is common knowledge that providing disperse systems such as emulsion particles with uniform diameters increases viscosity and makes it impossible to obtain high-concentration products. The increase in viscosity is particularly pronounced in hollow particles, in which water or organic solvents are contained inside the particles.

[0010] In view of the above, the conventional idea of uniform particle diameters was reconsidered, and a surprising discovery was made. Namely, it was discovered that an emulsion system obtained by adding small particles to a hollow-particle emulsion having uniform particle diameters is such that there is no reduction in the gloss, opacity, or other attributes of the hollow particle and that, on the contrary, the aforementioned viscosity under high shear is markedly reduced. Additional research was conducted, and the present invention was perfected. Specifically, the present invention provides emulsion particles that are characterized by comprising a group of hollow particles in which voids are present inside the particles during drying, and additionally comprising a group of smaller particles, and by the fact that the particle diameter distribution is bimodal. Adopting such a structure resolves the aforementioned problems of impaired paintability and drying properties without adversely affecting the superior

gloss, opacity, whiteness, light weight, and heat insulation of hollow particles.

[0011] Described below are examples of methods that can be used to manufacture emulsion particles having a bimodal distribution, which is a distinctive feature of the present invention.

(1) According to a conventional method for manufacturing hollow particles, small-diameter particles are produced as secondary particles midway through polymerization.

(2) According to a conventional method for manufacturing hollow particles, emulsion particles prepared in advance are added to form small-diameter particles midway through polymerization.

(3) According to a conventional method for manufacturing hollow particles, emulsion particles prepared in advance are added and small-diameter particles are introduced after polymerization has been completed.

[0012] Methods other than those cited above may also be used without any particular restrictions as long as these methods can produce the desired bimodal particle diameter distribution. Following is a detailed description of method (1), in which small-diameter particles are produced as secondary particles during polymerization.

(1)–1. The vinyl monomer remaining in an aqueous phase is polymerized and secondary particles are formed such that the balance between the rate of addition of the vinyl monomer and the polymerization rate thereof is upset, and the rate of addition is set much higher than the polymerization rate.

(2)–2. New particle nuclei consisting of a vinyl monomer are produced and small particles are formed by reducing the number of particles in the system, that is, reducing the number or surface area of sites at which the subsequently added and polymerized vinyl monomer is polymerized.

(1)–3. A surfactant is added in excess, either singly or together with a vinyl monomer, as a vinyl monomer emulsifier midway through polymerization, new particle nuclei are produced, and small particles are formed.

[0013] Known methods for manufacturing hollow emulsion particles can thus be modified to produce emulsion particles that comprise a group of hollow particles in which voids are present inside the particles during drying, that additionally comprise a group of smaller particles, and that have a bimodal particle diameter distribution. The shape of the hollow particles is not limited in any particular way. According to the applications (JP (Tokugan) 3-26678 and the like) previously filed by the inventors, however, better results are obtained with cored multilayer

particles which have core particles in their interior and in which a hollow layer is contained in the external-layer portion of each core particle.

[0014] The small particles accompanying the aforementioned group of hollow particles may be hollow particles, solid particles, or a mixture of the two. In this case, the diameter D of the hollow particles is commonly 0.3 to 5.0 μ , preferably 0.3 to 3.0 μ , and ideally 0.4 to 1.5 μ , whereas the diameter D_s of the small particles is commonly 0.05 to 0.3 μ , and preferably 0.08 to 0.25 μ . The inequality $D_s < D$, and preferably $D_s < D/2$, should always holds true.

[0015] The above-described drawbacks of conventional hollow particles are thus overcome by the use of emulsion particles that comprise a group of hollow particles in which voids are present inside the particles during drying, that additionally comprise a group of smaller particles, and that have a bimodal particle diameter distribution. These particles are obtained in accordance with the present invention in the manner described above and can, in particular, be used as plastic pigments in a variety of applications. In the particular case of paper coating compositions (paints), adding a trace amount of small particles is extremely beneficial in improving the applicability of the compositions at high speeds. In addition, admixing small particles makes it possible to prepare a high-concentration emulsion and to achieve better drying properties and lower cost without compromising the existing level of gloss, opacity, whiteness, or the like.

[0016] Following is a description of a paper coating composition (paint) containing emulsion particles that comprise a group of hollow particles in which voids are present inside the particles during drying, that additionally comprise a group of smaller particles, and that have a bimodal particle diameter distribution in accordance with the present invention. The paper coating composition (paint) of the present invention consists of the above-described emulsion particles as an inorganic pigment, as well as a binder and an inorganic pigment, and contains optionally added dispersants, antifoaming agents, mold release agents, viscosity modifiers, bluing agents, and the like. The binder may be a styrene-butadiene synthetic resin latex, acrylic synthetic resin emulsion, acryl-styrene synthetic resin emulsion, vinyl acetate synthetic resin emulsion, or other water-dispersible binder, or starch, modified starch, casein, polyvinyl alcohol, or another water-soluble binder. These binders may be used singly or as combinations of two or more components. In particular, styrene-butadiene synthetic resin latexes should preferably be used singly or together with starch, casein, or the like. In this case, the amount in which the binder is used should be 4 to 40 wt%, and preferably 6 to 20 wt%, in relation to total amount of the pigment (which consists of an inorganic pigment and a plastic pigment composed of the above-described emulsion particles). Using less than 4 wt% binder fails to produce a coating layer of practical strength. Using more than 40 wt%, on the other hand, fails to afford the desired gloss, opacity, or whiteness. Examples of such inorganic pigments include kaolin, calcium carbonate, talc, satin white, and titanium dioxide.

[0017] In this case, the amount in which the above-described emulsion particles are used, while not subject to any particular limitations as long as it is at least 1 wt% of the entire pigment amount, is preferably 2 to 70 wt%, and ideally 3 to 30 wt%. When added in an amount of less than 1 wt%, the above-described emulsion particles have no noticeable effect. The pH is adjusted to 7 or higher with a basic substance in order to stabilize the system during the mixing of the aforementioned binders, inorganic pigments, and emulsion particles. Sodium hydroxide, potassium hydroxide, or another inorganic basic substance should preferably be used because of considerations related to paint viscosity. The paper coating composition (paint) containing the plastic pigment of the present invention is applied to paper or paperboard with the aid of a blade coater, roll coater, gate roll coater, air knife coater, bar coater, or other common apparatus.

[0018] The resulting paper coating composition (paint) containing emulsion particles (these particles consist of a group of hollow particles in which voids are present inside the particles during drying, additionally consist of a group of smaller particles, and have a bimodal particle diameter distribution) in accordance with the present invention is characterized by having excellent gloss, opacity, and whiteness. The composition is also characterized by overcoming the drawbacks of conventional hollow particles, such as an increase in the moisture content of the paint or the reduced applicability at high speeds due to increased viscosity under conditions of high shear. This composition can be applied to common coated paper, paperboard, lightweight coated paper, ultra-lightweight coated paper, art paper, super-art paper, cast paper, and other types of paper.

[0019]

[Working Examples] Specific working examples of the present invention will now be described, but the present invention is not limited by these working examples alone. As used herein, "parts" and "%" refer in all cases to parts by weight and percent by weight, respectively. The shape, diameter, hollow layer or void diameter, and all other attributes of the emulsion particles prepared according to the examples were directly measured using a transmission electron microscope.

[0020] (I) Preparation of Emulsion Particles

Particle Example 1

Water (365 parts) was introduced into a separable flask equipped with a stirrer, a thermometer, and a reflux condenser; and the system was heated to 70°C while replaced with nitrogen under agitation. The internal temperature was kept at 70°C; potassium persulfate (0.4 part) was added as a polymerization initiator; the components were dissolved; 5% of the entire amount of an emulsion prepared in advance by adding vinyl monomer (a) (which consisted of 98 parts styrene,

2 parts 2-hydroxyethyl methacrylate, and 5 parts divinylbenzene) to 40 parts water and 0.05 part sodium lauryl sulfate were then introduced into the separable flask under agitation; the system was polymerized for 30 minutes; the remaining emulsion was added over a period of about 2 hours; a reaction was allowed to occur; and the product was aged for about 2 hours after all the emulsion had been added, yielding a core-particle emulsion with a particle diameter ϕ of 0.18 μ and a nonvolatile content of about 20%. This core-particle emulsion (137.3 parts) and water (959 parts) were then introduced into the same separable flask, and the system was heated to 78°C while replaced with nitrogen under agitation. The internal temperature was kept at 78°C; ammonium persulfate (0.1 part) was added as a polymerization initiator; the components were dissolved; an emulsion prepared in advance by adding vinyl monomer (b) (which consisted of 12.4 parts methyl methacrylate and 4.1 parts methacrylic acid) to 9.6 parts water and 0.1 part sodium lauryl sulfate was then continuously added and reacted under agitation over a period of 30 minutes, and the product was aged for 2 hours after all the emulsion has been added. Ammonium persulfate (0.9 part) was then added for the second time; the components were dissolved; an emulsion prepared in advance by adding vinyl monomer (c) (which consisted of 140 parts methyl methacrylate, 31.5 parts styrene, and 3.5 parts methacrylic acid) to 72 parts water and 0.6 part sodium lauryl sulfate under agitation was then continuously added and reacted over a period of 2 hours, and the product was aged for 2 hours after all the emulsion had been added.

[0021] After the polymerization had been completed, the internal temperature was raised to 90°C, 28% ammonia water (13.9 parts) was added under agitation, the pH was brought to 10.2, and agitation was continued unchanged for 10 minutes. Ammonium persulfate (4.4 parts) was then added for the second time while the internal temperature was kept unchanged at 90°C; the components were dissolved; an emulsion prepared in advance by adding vinyl monomer (d) (which consisted of 870 parts styrene and 9 parts acrylamide) to 360 parts water and 3.6 part sodium lauryl sulfate under agitation was then continuously added and reacted over a period of 2 hours, and the product was aged for 2 hours after the addition had been completed. The resulting emulsion particles were a mixture of hollow particles having a particle diameter D' of 0.2 μ and a void diameter of 0.1 μ with cored multilayer emulsion particles having a particle diameter D of 0.68 μ , a void layer diameter d of 0.50 μ , and a core particle diameter ϕ of 0.18 μ m.

[0022] Particle Example 2

Polymerization was performed by the same method as in Particle Example 1 except that the time during which vinyl monomer (b) was added in Particle Example 1 was changed to 3 hours, 10 parts of a solid styrene particle emulsion (solids: 40%) with a particle diameter of $0.08\ \mu$ were added after the polymerization of vinyl monomer (c) was completed, and 28% ammonia water was then added. The resulting emulsion particles were a mixture of solid particles having a particle diameter D' of $0.15\ \mu$ and cored multilayer emulsion particles having a particle diameter D of $0.67\ \mu$, a void layer diameter d of $0.50\ \mu$, and a core particle diameter ϕ of $0.18\ \mu\text{m}$.

[0023] Particle Example 3

Polymerization was performed by the same method as in Particle Example 2 except that the amount in which water was introduced in Particle Example 2 was changed from 959 parts to 680 parts, and the amount in which the solid styrene particle emulsion with a particle diameter of $0.08\ \mu$ was added after the polymerization of vinyl monomer (c) had been completed was changed to 50 parts. The resulting emulsion, obtained in an amount of 46.8%, was a mixture of solid particles having a particle diameter D' of $0.21\ \mu$ and cored multilayer emulsion particles having a particle diameter D of $0.66\ \mu$, a void layer diameter d of $0.48\ \mu$, and a core particle diameter ϕ of $0.18\ \mu\text{m}$.

[0024] Particle Example 4

Polymerization was performed by changing the addition time of the vinyl monomer (b) used in Particle Example 1 to 3 hours, and 1 part of a solid styrene particle emulsion (solids: 45%) having a particle diameter of $0.08\ \mu$ was mixed with 100 parts of the resulting cored multilayer emulsion particles (particle diameter D : $0.69\ \mu$; void layer diameter d : $0.50\ \mu$; core particle diameter ϕ : $0.18\ \mu\text{m}$; solids: 42%), yielding emulsion particles of Particle Example 4.

[0025] Particle Example 5

Water (350 parts) and sodium hydrogen carbonate (1.5 parts) were introduced into the same separable flask as in Particle Example 1, and the system was heated to 70°C while replaced with nitrogen under agitation. The internal temperature was kept at 70°C ; potassium persulfate (3.0 parts) was added as a polymerization initiator; the components were dissolved; an emulsion prepared in advance by adding 60 parts vinyl acetate, 80 parts butyl acrylate, 52 parts methyl methacrylate, 4 parts acrylic acid, and 4 parts acrylamide to 150 parts water and 0.1 part sodium lauryl sulfate under agitation was then continuously added and reacted over a period of 3 hours; and the product was aged for 1 hour after all the emulsion had been added. An emulsion

80nm .45

100 x .42 = 42 690nm

prepared in advance by adding 250 parts styrene, 125 parts butyl methacrylate, 15 parts acrylic acid, and 10 parts acrylamide to 300 parts water and 5 parts sodium lauryl sulfate under agitation was then continuously added and reacted over a period of 4 hours, and the product was aged for 2 hours after all the emulsion had been added. After the polymerization had been completed, 41.7 [parts] of a 20% aqueous solution of sodium hydroxide were added under agitation to the resulting emulsion, the pH of the emulsion was raised to 10.5, the temperature was increased to 95°C, and the agitation was continued unchanged for another 4 hours. A separately prepared solid styrene particle emulsion (solids: 50%) having a particle diameter of $0.2\ \mu$ was mixed in an amount of 50 parts with 100 parts of the resulting hollow emulsion particles, which had a particle diameter D of $0.91\ \mu$, an inside particle diameter of $0.62\ \mu$, and a solids content of 42%, yielding emulsion particles of Particle Example 5 that had a solids content of 44.7%. *200 μm*

Comparative Particle Example 1

Comparative Particle Example 1 involved obtaining cored multilayer emulsion particles having a particle diameter D of $0.69\ \mu$, a void layer diameter d of $0.50\ \mu$, and a core particle diameter ϕ of $0.18\ \mu$ by performing polymerization according to the same method as in Particle Example 1, except that the addition time of vinyl monomer (b) was changed to 3 hours. *0.69 μm*

Comparative Particle Example 2

Comparative Particle Example 2 was performed in the same manner as Particle Example 5, except that no solid styrene particle emulsion was added. *910 μm*

Comparative Particle Example 3

The same polymerization as in Particle Example 3 was performed, but without adding the solid styrene particle emulsion. Viscosity increased rapidly after the polymerization was completed, and the entire product had gelled, making it impossible to obtain an emulsion.

[0026] (II) Simplified Evaluation of Drying Properties and Covering Power of Emulsion Particles

The emulsions obtained in Particle Example 3 and Comparative Particle Example 1 were used. An acrylic synthetic resin emulsion (Almatex E-175, manufactured by Mitsui Toatsu Chemicals) was used as a binder. The emulsion particles obtained were added to the emulsion such that the weight ratio of the particles and the binder was 3/7, and the solids content was 40%. The product was applied by an applicator bar to a glass plate to obtain a 20- μ dry paint coat, and drying was visually monitored in an atmosphere with a temperature of 20°C and a humidity of 60%. The monitoring involved observing Size 4 newspaper text through the coated glass plate (the text was placed at a distance of 1 cm behind the plate), and grading text visibility according to the

following four-point system.

- [0027] 1: Excellent (Text invisible)
 2: Good (Text faintly visible)
 3: Fair (Text visible)
 4: Poor (Text clearly invisible)

The results are shown in Table 1.

[0028]

Table 1

Time elapsed, min	Particle Example 3	Comparative Particle Example 1
5	3	3
10	3	3
15	3	4
20	2	3
25	1*	2
30	1	1*
35	1	1
40	1	1

* Designates the time when constant opacity was visually determined.

[0029] (III) Preparation of Paper Coating Composition (Paint)

The resulting emulsion particles were evaluated for their performance as a plastic pigment for paper coating applications involving the following model composition.

Component	Dry weight
Kaolin clay (UW-90, manufactured by EMC)	63 parts
Calcium carbonate, light (TP-222HS, manufactured by Okutama Kogyo)	27 parts
Emulsion particles	10 parts
Dispersant (Aron T-40, manufactured by Toagosei Chemical)	0.09 part
Phosphoric acid esterified starch (MS-4600, manufactured by Nihon Shokuhin Kogyo)	3 parts
SBR latex (Polylac 755, manufactured by Mitsui Toatsu Chemicals)	13 parts
Paint solids	62%

To prepare a paint, Aron T-40 (solids: 40%) was added as a dispersant to water; UW-90 was thoroughly dispersed using a Cowles mixer; a slurry of the light calcium carbonate was added thereto, the components were thoroughly dispersed; and the emulsion particles, MS-4600, and SBR latex were then added to the dispersion. The pH of the paint was adjusted to 9 with sodium hydroxide.

[0030] The high-shear viscosity of the resulting paint was measured at 8800 rpm with a Hercules rheometer. At the same time, the paint was applied with an applicator to wood-free paper in a dry coating amount of 15 g/m², dried for 20 seconds at 120°C, and passed twice between calender rolls at a roll temperature of 60°C, a linear pressure of 70 kg/cm, and a speed of 10 m/min, yielding coated paper. This paper was evaluated in the following manner.

- High-shear viscosity: Measured by Hercules rheometer (8800 rpm)
- White paper gloss: Reflectivity at 75° was measured according to JIS P-8142
- Print gloss: 0.4 cc of New Bright Indigo (manufactured by Toyo Ink) was printed using an RI print tester. Following drying, reflectivity at 75° was measured according to JIS P-8142
- Degree of whiteness: Measured by a Hunter whiteness meter in accordance with JIS P-8123
- Degree of opacity: Measured in accordance with JIS P-8138

The results are shown in Table 2.

[0031]

Table 2

	Particles	High-shear viscosity (cP)	White paper gloss	Print gloss	Degree of whiteness (%)	Degree of opacity (%)
Working Example 1	Particle Example 1	34	73.3	88.4	81.8	89.6
Working Example 2	Particle Example 2	32	73.6	88.4	81.8	89.5
Working Example 3	Particle Example 3	28	73.4	88.3	81.7	89.5
Working Example 4	Particle Example 4	32	73.3	88.5	81.8	89.5
Working Example 5	Particle Example 5	29	70.9	87.1	80.6	88.0
Comparative Example 1	Comparative Particle Example 1	40	73.4	88.2	81.8	89.6
Comparative Example 2	Comparative Particle Example 2	43	70.8	86.9	80.5	88.1

[0032]

[Merits of the Invention] The emulsion particles of the present invention (whose distinctive feature is that they consist of a group of hollow particles in which voids are present inside the particles during drying, additionally consist of a group of smaller particles, and have a bimodal particle diameter distribution) not only have excellent gloss, opacity, and whiteness but also possess exceptional drying properties and solids concentration by weight, as well as improved paintability and low viscosity under high shear when added to a paper coating composition (paint). Such characteristics cannot be obtained with conventional hollow particle emulsions having uniform particle diameters.